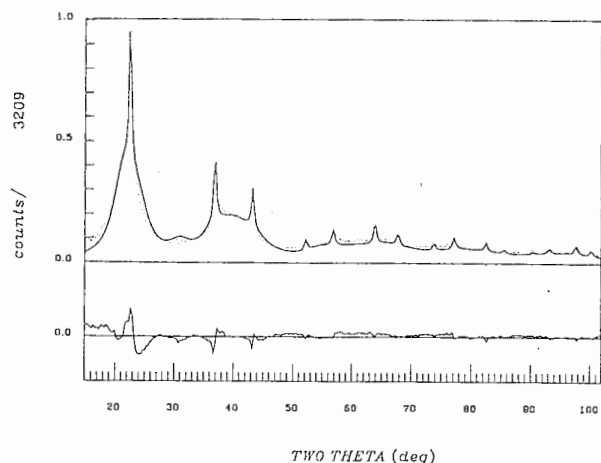


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In conclusion, fullerenes are stable when submitted to isotropic stress, but are squeezed by nonhydrostatic high pressures.  $C_{60}$  molecules contain a degree of  $sp^3$  as well as  $sp^2$  hybridization which could favor these different structural transformations and temperature is an important factor controlling the nature of the final phase.



MS-10.02.05 THE EXOHEDRAL CHEMISTRY OF FULLERENES, by R. M. Walton\*, School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, England, UK

Our knowledge of the factors affecting the exohedral chemical reactivity of  $C_{60}$  (Buckminsterfullerenes) and  $C_{70}$  in particular is slowly growing as the regioselectivity of additions to the cage begin to form a coherent picture. The current position will be reviewed in the context of recent results obtained at the University of Sussex.

PS-10.02.06 CRYSTALLOGRAPHIC COUNTING METHODS APPLIED TO FULLERENE CAGE ISOMERISM. J. S. Rutherford, Department of Chemistry, University of Transkei, South Africa.

The tessellation or lattice-projection method of generating fullerene structures considers the carbon cage to be formed from a graphite sheet by cutting, folding and gluing, during which process 12 hexagons are converted into the pentagons of the final cage. This approach provides a means to enumerate the cage isomers by symmetry, in what is essentially a counting of the corresponding two-dimensional derivative lattices.

This technique has already yielded the following results regarding possible cage isomers:

1. All fullerenes belong to infinite families,  $C_{nx}$ , with geometrically similar arrangements of the pentagons to that of a specific parent  $C_n$ , with  $x$  comprising the integral solutions of  $(h^2 + hk + k^2)$ .
2. The number of such solutions,  $N(x)$ , and their distribution by symmetry relative to that of the frame of pentagons, can be derived using Dirichlet generating functions.
3. The total number of cage stereoisomers of formula  $C_n$ , is roughly proportional to  $n^{10}$ .

PS-10.02.07

PREPARATION CONDITIONS OF CARBON NANOTUBES. By Yoshinori ANDO\*, Department of Physics, Meijo University, Tenpaku-ku, Nagoya 468, Japan, and Sumio IJIMA, Research and Development Group, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.

Carbon nanotubes are extremely thin filaments with helical tubular graphite structure (Iijima (1991). Nature **354**, 56, Ando and Iijima (1993). Jpn. J. Appl. Phys. **32**, L107) found in carbon deposits on the negative graphite electrode, formed during generation of fullerenes such as  $C_{60}$ . Recently, these nanotubes were used as moulds for the fabrication of metallic nanowires by capillary action (Ajayan and Iijima (1993). Nature **361**, 333). We report here on the preparation conditions of nanotubes in three kinds of atmospheres.

The evaporation of carbon has been carried out by dc arc discharge at about 220A between 10mm diameter graphite electrodes. He, Ar or  $CH_4$  at pressures of 10-200 Torr were used as the atmospheric gas, although it is known that fullerenes cannot be prepared in  $CH_4$ . The positive graphite electrode is consumed by evaporation. The evaporated carbon partially deposits on the negative electrode. This deposit was sectioned with a diamond saw and its surface was observed by high resolution SEM and TEM.

An example of SEM images obtained from the deposit produced by carbon evaporation in 50 Torr  $CH_4$  gas is shown in Fig. 1. A number of nanometer-size fibers and particles, called respectively "nanotubes" and "nanoparticles", are seen. The shape of nanoparticles is spherical, polyhedral or also elongated. Of course, the tubular structure of the fibers could be revealed only by high-resolution TEM.

The dependency on gas pressure is not very remarkable, but the proportion of carbon nanotubes in the deposit decreases with the decrease of gas pressure. Similar coexistence of nanotubes and nanoparticles could be found in deposits evaporated in atmospheres of He or Ar. On the other hand, fullerene formation is effective only in He gas environment, considerably reduced in Ar and absent in  $CH_4$ . The growth conditions of nanotubes and nanoparticles are therefore less restricted than those of fullerene.

## 10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

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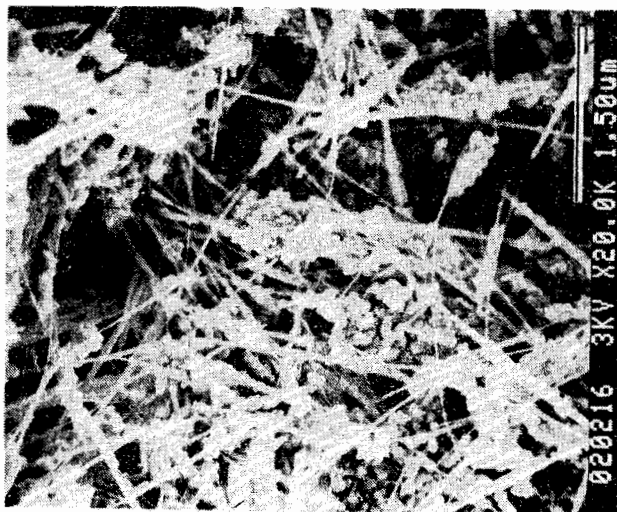


Fig. 1. SEM image of carbon deposit in 50 Torr CH<sub>4</sub>.

### PS-10.02.08 STRUCTURAL STUDY OF ORTHORHOMBIC C<sub>60</sub> CRYSTAL UNDER HIGH PRESSURE.

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In contrast to a well-known fcc C<sub>60</sub> crystal, a relatively large single crystal (0.1 x 0.5 x 5mm<sup>3</sup>) with an orthorhombic lattice was successfully grown from CS<sub>2</sub> solution (Kikuchi et al., 1991). Its structure was tentatively assigned to the space group Pbnm with its lattice constants a=24.99, b=25.60, c=10.00 Å (Z=8) under an ambient condition. In order to study its structural aspects under hydrostatic pressure, we have carried out x-ray diffraction experiments by using a diamond-anvil cell on both conventional laboratory source and synchrotron radiation source of the Photon Factory. With increasing pressure, we have discovered a phase transition from orthorhombic to monoclinic lattices between 1.1 and 2.2 GPa at room temperature. Upon the transition, the orthorhombic c-axis inclines in the ac plane by an angle of 0.55 deg. while other principal axes are retained. The pressure dependence of its unit cell volume (bulk compression) does not show appreciable discontinuity across the transition pressure and it is fitted by the Birch-Murnaghan equation of state resulting in its bulk modulus K<sub>0</sub>=10.5+1.9 GPa. This is contrast to the value of the fcc crystal (K<sub>0</sub>=18.1 GPa) (Duclos et al., 1991), showing that the orthorhombic crystal is much more compressible than the fcc one. However, we have not succeeded in obtaining information of molecular displacements associated with the

transition.

One of the present authors (SS) thanks Special Researchers' Basic Program, RIKEN. This synchrotron radiation x-ray diffraction experiment was carried out under the proposal approved by the PF-PAC (NO. 90-093).

DUCLOS, S.J., BRISTER, K., HADDON, R.C., KORTAN, A.R., & THIEL, F.A. (1991), *Nature* **351**, 380.

KIKUCHI, K., SUZUKI, S., SAITO, K., SHIROMARU, H., IKEMOTO, I. & ACHIBA, Y. (1991), *Physica C* **415**, 185-189.

PS-10.02.09 FORMATION OF CARBON NANOTUBES BY THE EVAPORATION OF CARBON ROD CONTAINING Sc<sub>2</sub>O<sub>3</sub> By Masato OHKOHCHI\*, Yoshinori ANDO, Department of Physics, Meijo University, Tenpaku-ku, Nagoya 468, Japan, Shunji BANDO, Inst. Molec. Sci., Myodaiji, Okazaki 444, Japan and Yahachi SAITO, Mie University, Uehama, Tu 514, Japan

Gas evaporation method using dc arc-discharge has been applied to form fullerenes, i.e. carbon 60 and relatives. When the fullerenes are formed by this method, carbonaceous deposits are formed onto the tip of negative electrode. It is well known that there exist carbon nanotubes and nanoparticles in the deposits (Iijima, *Nature* 1991, 354, 56, Ando and Iijima, *Jpn. J. Appl. Phys.*, 1993, 32, L107). Recently, the experiment of metal encapsulated fullerenes has become interested from the viewpoint of physical properties. When the positive carbon electrode is replaced to carbon rods containing metal, metal encapsulated fullerenes are formed (Shinohara et al., *Nature*, 1992, 357, 52.). Here, we carried out arc-discharge by the use of carbon rods containing Sc<sub>2</sub>O<sub>3</sub> on the positive electrode, and observed by high resolution SEM carbon nanotubes and nanoparticles growing in the carbonaceous deposits. From the result, we discuss Sc effect on the growth of the tube.

On the negative electrode side, the high purity graphite rod of 10mmφ was used. On the other hand, three kinds of carbon rods (containing Sc<sub>2</sub>O<sub>3</sub> and pitch, containing pitch only and pure graphite containing nothing) were used on the positive electrode to compare difference of the nanotube growth brought about by composition of original carbon rod. The atmospheric gas used in the experiment was helium gas of 50 Torr. Dc arc electric current was varied in the range from 180A to 260A. The deposits formed by this evaporation were cut by diamond saw, and the cross section was observed by SEM.

The feature of nanotubes in the deposit formed by evaporation of a rod containing Sc<sub>2</sub>O<sub>3</sub> and pitch is shown in Fig. 1. The amount of nanotubes is tremendous. Many nanotubes with same diameter are bundled together to form long wavy fibres. On the other hand, in the case of rods without Sc<sub>2</sub>O<sub>3</sub>, the nanotubes are straight and not so bundled. Also, many more nanoparticles than bundles are observed in this case. From these observations, it became clear that Sc had a great effect on the growth of nanotubes.